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A new synthesis of $FOClO_3$ was discovered involving the fluorination of ClO_4^- with ClF_6^+. An unexpected oxygen abstraction from ClF_4O^- was observed when $CsClF_4O$ was reacted with $FOSO_2F$.

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TECHNICAL REPORT NO. 4

Some Interesting Observations in Chlorine Oxyfluoride Chemistry

by

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SOME INTERESTING OBSERVATIONS IN CHLORINE OXYFLUORIDE CHEMISTRY

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SUMMARY

A new synthesis of $FOClO_3$ was discovered involving the fluorination of ClO_4^- with ClF_6^+. An unexpected oxygen abstraction from ClF_4O^- was observed when $CsClF_4O$ was reacted with $FOSO_2F$.

INTRODUCTION

We would like to report two interesting reactions observed during our studies in the area of chlorine oxyfluorides. The first reaction involved the low-temperature metathesis of ClF_6AsF_6 with $CsClO_4$ in anhydrous HF solution. In view of the known NF_4^+ reaction [1]

$$NF_4SbF_6 + CsClO_4 \xrightarrow[-45°C]{HF} CsSbF_6 + NF_4ClO_4$$

$$NF_4ClO_4 \xrightarrow{25°C} NF_3 + FOClO_3$$

it was interesting to study whether ClF_6^+ is also capable of

oxidizing ClO_4^- to $FOClO_3$. The thermal stability of ClF_6ClO_4 was found to be lower than that of NF_4ClO_4[1] and did not permit the isolation of solid ClF_6ClO_4 even at temperatures as low as -45°C. However, the corresponding decomposition products, $FOClO_3$ and ClF_5, were observed in good yield.

$$ClF_6AsF_6 + CsClO_4 \xrightarrow[-45°C]{HF} CsAsF_6\downarrow + [ClF_6ClO_4]$$

$$[ClF_6ClO_4] \longrightarrow ClF_5 + FOClO_3$$

Although this presents an alternative synthetic path to $FOClO_3$, the NF_4^+ reaction is preferred from a synthetic point of view since the NF_4SbF_6 starting material is more readily accessible [2].

The second reaction involved $CsClF_4O$ and $FOSO_2F$. Fluorine fluorosulfate is known to be a useful reagent for the synthesis of hypofluorites [3], such as

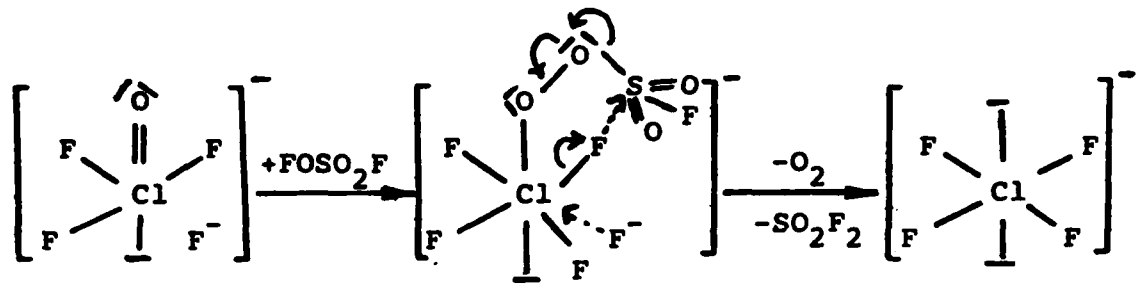
$$CsTeF_5O + FOSO_2F \longrightarrow CsSO_3F + TeF_5OF$$

For $CsClF_4O$, however, the major reaction was not the formation of either the unknown ClF_4OF or its expected decomposition products, but oxygen abstraction accompanied by SO_2F_2 elimination according to the following reaction.

$$CsClF_4O + FOSO_2F \longrightarrow CsClF_4 + SO_2F_2 + O_2$$

This unexpected reaction path might be rationalized in terms of an addition of $FOSO_2F$ to the Cl=O bond in one of the favored resonance structures of ClF_4O^-[4], followed by an intramolecular

nucleophilic substitution (S_N1) reaction accompanied by O_2 and SO_2F_2 elimination:



To our knowledge, this is the first example of a reaction in which $FOSO_2F$ acts as a deoxygenating agent.

EXPERIMENTAL

Apparatus. Volatile materials were handled in a stainless steel-Teflon FEP vacuum line [5]. The line and other hardware used were well passivated with ClF_3 and, if HF was to be used, with HF. Nonvolatile materials were handled in the dry nitrogen atmosphere of a glovebox. Metathetical reactions were carried out in HF solution using a previously described apparatus [6].

Infrared spectra were recorded on a Perkin Elmer Model 283 spectrophotometer. Spectra of solids were obtained using dry powders pressed between AgCl windows. Spectra of gases were obtained by using a Teflon cell of 5 cm path length equipped with AgCl windows. Raman spectra were recorded on a Cary Model 83 spectrophotometer using the 4880-Å exciting line of an Ar-ion laser.

Materials. Literature methods were used for the syntheses of ClF_6AsF_6[7], $CsClF_4O$[8] and $FOSO_2F$[9] and for the drying of

the HF solvent [10]. The $CsClO_4$ (ROC/RIC) was used as received.

Reaction of ClF_6AsF_6 with $CsClO_4$. In the drybox ClF_6AsF_6 (0.318 mmol) and $CsClO_4$ (0.304 mmol) were placed into the bottom U-tube of the metathesis apparatus [6]. On the vacuum line, dry HF (1.1 ml of liquid) was added at -78°C. The resulting mixture was agitated at -45°C for 1.5 hr and then filtered at -78°C through a porous Teflon filter while the filtrate was collected at -45°C. All material volatile at -45° was pumped off for 2.5 hr and separated by fractional condensation through a series of traps kept at -126, -142 and -196°C. The -126° trap contained the HF solvent and a small amount of $FClO_2$, the -142° trap contained a mixture of $FOClO_3$ and ClF_5 (0.445 mmol), and the -196° trap contained $FClO_3$ (0.128 mmol). Essentially no filtrate residue was left behind. The white solid filter cake (106 mg, weight calcd for 0.304 mmol of $CsAsF_6$ 98 mg) was identified by infrared and Raman spectroscopy as $CsAsF_6$. The $FClO_3$ formed in the above reaction is attributed to decomposition of a small amount of $FOClO_3$. For a larger scale reaction, the percentage of $FClO_3$ in the product is expected to decrease significantly.

Caution! Fluorine perchlorate is highly shock sensitive [11] and proper safety precautions must be taken when working with this material.

Reaction of $CsClF_4O$ with $FOSO_2F$. In the dry box $CsClF_4O$ (2.24 mmol) was placed into a 10 ml stainless steel cylinder. On the vacuum line $FOSO_2F$ (4.97 mmol) was added to the cylinder at -196°C. The cylinder was kept at 0°C for 3 days, then cooled

to -196°C. Oxygen (2.23 mmol) was pumped off at -196°C, and all material volatile at ambient temperature was separated by fractional condensation through traps kept at -112, -142, and -196°C. The -112° trap contained small amounts of ClF_3O, $FClO_2$ and ClF_3. The -142° trap contained $FOSO_2F$ (2.6 mmol) and SO_2F_2 (1.7 mmol), and the -196° trap showed SO_2F_2 (0.52 mmol). The white solid residue showed a weight loss of 39 mg (calcd weight loss for 1.12 mmol of O_2 36 mg) and was identified by infrared and Raman spectroscopy as $CsClF_4$ [12] containing a small amount of $CsSO_3F$.

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